

COPROCESSING - THE HYDROGENATION OF LIGNITE TOGETHER WITH RESIDUAL OILS

Uwe Lenz, Joachim Wawrzinek *
Axel Giehr**

* Rheinische Braunkohlenwerke AG, D 5000 Köln 41

**Union Rheinische Braunkohlen Kraftstoff AG, D 5047 Wesseling

1 ABSTRACT

The current overflow on the crude oil market must not obscure the fact that world oil resources are limited. Instead, it must be our goal to develop practicable concepts for the conversion of fossil raw materials and optimize their economic viability. The joint development programme of the Rheinische Braunkohlenwerke AG and the Union Rheinische Braunkohlen Kraftstoff AG for the catalytic hydrogenation of fossil raw materials in the liquid phase aims at this goal.

In a continuously operating process development unit extensive investigations have been carried out focussing on:

- conversion of lignite,
- development of catalysts based on lignite coke,
- conversion of heavy residual oils,
- conversion of mixtures of lignite and residual oils (coprocessing).

In this paper the results of these investigations are discussed.

A comparison of lignite liquefaction and coprocessing elucidates the advantage of coprocessing. Thanks to a change in the process route and a yield-improving synergistic effect, coal liquefaction via coprocessing will reach economic viability earlier than the liquefaction of coal alone.

2 RESEARCH AND DEVELOPMENT PROJECTS TO CONVERT FOSSIL RAW MATERIALS

In view of the future situation in the crude oil market where oil less in quantity and quality will be available it is necessary to develop practicable concepts for the conversion of fossil fuels.

In the field of refining, e.g., there are several processes permitting the conversion of heavy residual oils or even extra-heavy crude oils into lower-boiling products. Some of these processes have for quite some time been applied on an industrial scale; they include coking, deasphaltization, and H-oil processes. Limiting factors in respect of process application are the quality of feed oils (content of heavy metals) and/or the quality of by-products (petrol coke).

The process suitable for use in a much wider field of application is the conversion of fossil fuels in liquid-phase hydrogenation; it is based on coal liquefaction according to Bergius-Pier, a process which can look back on many years of application. In our group, e.g., it was used from 1941 to 1964 to process lignite and heavy oil on a commercial scale.

The development programme on which the Rheinische Braunkohlenwerke AG (Rheinbraun) and the Union Rheinische Braunkohlen Kraftstoff AG (Union Kraftstoff) have been cooperating since 1978 and which deals with the hydrogenation of fossil fuels to make high-grade liquid hydrocarbons centres around the following:

- hydroliquefaction of lignite,
- hydroliquefaction of residual oils,
- hydroliquefaction of mixtures of lignite and residual oils (coprocessing),
- development of suitable catalysts based on lignite coke.

In its first stage, i.e. on a process-development scale, we implement the development programme with the aim of

- further developing and optimizing the processes applied from 1941 to 1964,
- determining process data,
- finding out whether hydrogenation of fossil fuels will be economically viable.

Major fields of these projects were and are financially supported by the Federal Ministry of Research and Technology.

In the following, this paper will deal not only with the results obtained in the investigations of coprocessing; in order to facilitate understanding of this subject, it will also discuss the results which are achieved in the investigations of lignite liquefaction, hydrogenation of residual oils, and development of catalysts.

3 FUNDAMENTAL PROCESS DIFFERENCES IN THE CASE OF HYDROGENATION OF COAL, MIXTURES AND RESIDUAL OILS

Between coal liquefaction, on the one hand, and hydrogenation of mixtures and residual oils, on the other hand, there is a major difference in process engineering (Figure 1). Today, conversion of residues and coprocessing are generally operated in a "once-through mode"; contrary to this, coal liquefaction calls for cycling of the slurry oil, and the operating mode preferably used to hydrogenate residual oils in the commercial-scale plants until 1964 was recycling of the cold separator heavy oil and parts of the hot separator sludge. Since recycling is no longer required, coprocessing - contrary to coal hydrogenation - permits a major simplification of the process route. In coprocessing, the mineral oil-derived residual oil acts as slurry oil which is converted into lower-boiling products without any cycling being required.

Due to today's advanced refining technique it is advisable not to recycle the heavy oil produced during hydrogenation, but to hydrocrack it and produce naphtha and gas oil for use in the motor fuel sector or feedstocks for use in petrochemistry.

The liquid-phase process benefits from the "once-through mode"; here, the reaction zone is not filled with cycled heavy oil and, hence, permits full charge with heavy oil.

4 TEST INSTALLATION

SET-UP AND OPERATION OF THE PROCESS DEVELOPMENT UNIT

Figure 2 shows the set-up of the test plant for lignite hydroliquefaction.

This plant is also used to carry out tests on conversion of heavy residual oils and coprocessing.

The plant is designed for fully continuous operation.

The feedstock is predried powdered lignite with a residual water content of up to 12% wt and a maximum grain size of 1 mm and/or oil with an initial atmospheric boiling point of $> 510^{\circ}\text{C}$.

The reaction pressure of hydrogenation ranged between 150 and 300 bar.

The reactor has a volume of approx. 8 l. Two reactors with an inner diameter of 4.5 cm each are connected in series. The pumps are designed for an hourly

throughput of coal slurry or oils of up to 16 l/hr.

The average availability of the plant was 60% for hydrogenation on the basis of coal while it rose to more than 80% for hydrogenation with residual oil.

5 LIGNITE HYDROLIQUEFACTION

5.1 RESULTS OBTAINED DURING TESTS IN THE PROCESS DEVELOPMENT UNIT

Within the scope of the lignite hydroliquefaction projects we performed, from 1978 to 1983, extensive development work in that process development unit.

In the following, the major results are summarized.

Yields as a function of temperature and gas throughput

In the temperature range under investigation, the oil yields as a function of temperature rise from 41 to 48 parts by weight. The residue portion decreases from 28 to 18 parts by weight, and the amount of hydrocarbon gases produced rises from 13 to 26 parts by weight, each related to 100 parts by weight at a coal throughput, maf, of 0.5 to 0.6 kg/l x hr.

Through an increase in the cycle gas amount of 30% the oil yield rises to approx. 53 parts by weight in the temperature range under investigation, while only some 12 parts by weight (Figure 3) will be obtained as residue.

It has not yet been possible to make definite statements about whether an increase in the amount of cycle gas will also produce higher yields in commercial-scale reactors with different fluid dynamics conditions.

Yield as a function of pressure

The tests in the process development unit have shown that at a pressure of 220 bar and with the same linear flow velocity as at 300 bar - for this, the volume of cycle gas was reduced from 18 to 14 m³/hr - the oil yield decreases by 3 parts by weight as a result of the lower pressure. The portion of residue increases by the same amount. In the temperature range under investigation, the hydrocarbon gases correspond to the comparative values at 300 bar.

At a pressure of 150 bar and with the same cycle gas velocity as at 300 bar (9 m³/hr) the process development unit yields an amount of oil which is about 10 parts by weight lower.

Recycling of supercritical fluid (SCF) extract

Thanks to the high extract yields, the supercritical fluid extraction technique produced considerably higher oil amounts and lower portions of residue than would be obtained, if conventional vacuum distillation of the sludge were employed under the same conditions. Figure 4 shows a comparison of the yields.

A final judgement on this technique can only be given when the test results to be obtained in a pilot plant will be on hand.

Sludge recycling

A crucial problem in hydroliquefaction is the formation of CaCO₃ containing sediments which give rise to coking.

Since part of the hot separator sludge (approx. 20% of the slurry oil) was recycled into the reaction zone, we were able to prevent cokings and deposits in the reactors of the process development unit; this was due to an improved fluid dynamics resulting from a better "carrying capacity" of the reaction mixture which in turn was caused by a rise in density.

The yields correspond to comparative figures obtained without sludge recycling.

5.2 PROCESS CONCEPT

The process concept of lignite hydroliquefaction consists of the following steps:

- coal drying and slurrying,
- hydrogenation in the liquid phase at pressures between 200 and 300 bar,
- partial cycling of sludge from the hot separator to the slurry oil,
- separation of the remaining hot separator product by way of distillation or supercritical fluid extraction into a solids-free oil for slurrying and a residue for hydrogen production,
- use of H_2S as co-catalyst, and
- coal-oil refining.

The question of whether this process concept can be implemented on a commercial scale has to be cleared up in two development stages, i.e. first in a pilot plant, and then in a demonstration plant where its industrial-scale feasibility and its economic viability are to be verified.

The results we obtained during operation of the process development unit formed a basis for the basic engineering and authority permittance required for a lignite hydrogenation pilot plant. In mid-1983, the competent authority granted the building and operating licences for a plant designed for an hourly coal throughput of up to 25 t (t - tonne) and to be located on the grounds of the Union Kraftstoff.

Due to economic considerations construction of this pilot plant has been postponed because the current price of gasoline produced by lignite hydrogenation is still about two times as high as that of petroleum-derived gasoline.

6 HYDROLIQUEFACTION OF RESIDUAL OILS

Within the scope of the project dealing with residual oil hydrogenation we carried out investigations in the process development unit with the aim of:

- clearing up the mode of action of liquid-phase catalysts and developing a suitable catalyst on the basis of lignite products, and
- determining yields and product qualities when different residual oils are used.

6.1 DEVELOPMENT OF CATALYSTS

From 1948 to 1964 when the commercial-scale liquid-phase plant worked with atmospheric distillation and cracking residues, entrained dust from lignite gasification was used as a base material for developing catalysts. With the addition of ferrous salts this material constituted an efficient and low-priced disposable catalyst.

Since today such or similar products from lignite gasification are either no longer available or occur in such small quantities that are insufficient to meet commercial-scale requirements, tests were made to develop a suitable

and low-priced substitution product which is likewise derived from lignite products.

The result we obtained in the extensive research work on catalyst development showed that the following materials are particularly suitable:

- entrained dust from High-Temperature Winkler gasification,
- powdered coke from the rotary-hearth furnace process (rotary-hearth furnace coke),
- steam-activated rotary-hearth furnace coke.

For economical reasons, rotary-hearth furnace coke is preferably used (Figure 5).

The previous tests have shown that the catalysts influence not only the yield structure, but also the performance of the hydrogenation plant. A troublefree long-time performance without any temperature inhomogeneity and coke deposits in the reactors was only obtained when a lignite coke-derived catalyst was added.

Thanks to the successful research work described above we can now provide sufficient quantities of highly suitable and low-priced catalysts for coprocessing and liquid-phase hydrogenation of residual oils.

Mode of action of liquid-phase catalysts

The lignite-based solid matter which is added as catalyst to the liquid-phase process passes slowly through the reactors and is subsequently discharged from the hot separator.

Investigations of this solid matter have shown that due to its surface properties the catalyst used serves as an adsorbent for asphaltenes and carries them out of the reaction zone, thus preventing coking and coke deposits there. We discovered that in this way up to 1% wt of the residual oil fed was discharged along with the catalyst from the process cycle. As electron-microscopical analyses have shown, major part of the catalyst surface is preserved in this process.

Figure 6 compares the X-ray fluorescence analysis of the solid matter isolated from the hot separator sludge with that of powdered coke.

For powdered coke, only the components of lignite ash are indicated. In the electron-microscopical analysis of the solid matter leaving the hot separator, the heavy metals, nickel and vanadium, occur in addition. This is an indication that apart from asphaltenes the liquid-phase catalyst also adsorbs the heavy metal components in the residual oil. Taking-up of the transition metals with hydrocracking activities allows the catalyst to step up its catalytic activity in the liquid phase.

From the catalytic properties of the coke alone, after having been "activated" in the liquid phase and with account taken of the capturing effect on asphaltenes, we can derive the following model representation of the catalyst's mode of action:

- the catalyst on the basis of lignite coke has a hydrocracking effect because of its surface properties and its mineral composition;
- due to the absorption of nickel and vanadium the catalyst on the basis of lignite coke reaches its maximum catalytic activity in the liquid phase;
- due to its surface properties the catalyst on the basis of lignite coke acts as an adsorbent on potential coke precursors and carries them out of the reaction zone; thus, it prevents coking and coke deposits there, and

- under the reaction conditions of liquid-phase hydrogenation the catalyst on the basis of lignite coke has a similar fluid-dynamics behaviour to that of the residual oil; it is discharged in an "once-through mode".

6.2 RESULTS OBTAINED WITH DIFFERENT RESIDUAL OILS

The chemical and physical properties of heavy residual oils strongly vary depending on their crude oil origin. Thus, different yields and product qualities are obtained depending on what feedstock is used in liquid-phase hydrogenation of heavy residual oils. Against this background, we conducted an investigation with the object of determining yields and product qualities for a variety of residual oils with most different chemical compositions and, in addition, defining optimum reaction conditions and operating modes in the process development unit.

Figure 7 classifies the different residual oils by their heavy metal contents and the prevailing type of hydrocarbons they contain.

Of the crude oil types classified in Figure 7, we investigated vacuum and visbreaking residues in the process development unit. In doing so, we focussed our activities on the investigation of asphaltene-rich residues since these matters would chiefly be processed in an industrial-scale plant.

The results we obtained in this extensive investigation can be summarized as follows:

- depending on the residual oil used the conversion rates obtained ranged between 70% and 95%;
- under optimized reaction conditions, the oil yields were between 60 and 85% wt; the residue decreased to amounts between 5 and 23% wt; depending on the feedstock, the yield of hydrocarbon gases was 5 to 15% wt;
- under the same reaction conditions, vacuum residues produced higher oil yields than corresponding visbreaking residues; since it was possible to convert visbreaking residues under more severe reaction conditions than vacuum residues, we obtained comparable yield distributions from both products;
- residual oils rich in asphaltene and heavy metals showed a smaller tendency towards coking in the reactors than naphthene- and paraffin-rich residual oils with lower heavy metal contents.

7 COPROCESSING RESULTS

Within the scope of the coprocessing investigations, it was examined whether mixtures of dry lignite and residual oils can be processed under liquid-phase conditions as well.

The tests in the process development unit demonstrated the technical feasibility of coprocessing; in this case, approx. 30% of the vacuum residue was replaced by dry lignite; but almost the same yield distribution was obtained.

Under optimal conditions, coprocessing yielded conversion rates of about 90%. In the temperature range under study and with different reactor throughputs, we obtained oil yields of approx. 80% wt and portions of hydrogenation residue and hydrocarbon gases amounting to approx. 10% each.

In addition it was found that in the case of coprocessing and, in particular, with small reactor throughputs the absolute values of oil yields obtained from the mixture were higher than the comparative amounts in residual oil hydrogenation. It is an unexpected result since with approx. 48% wt the oil yields in conventional lignite liquefaction are much lower than those obtained in residual oil conversion. So, if the oil yields from coprocessing

were calculated theoretically, the resulting values would be always lower than those in residual oil hydrogenation. This result is shown in Figure 8.

The bar graph shows yields which were obtained under equal reaction conditions in residual oil hydrogenation, coprocessing and lignite liquefaction. In the case of coprocessing, we specified not only the figure of the yield distribution determined experimentally in the process development unit, but also the result obtained theoretically.

Figure 8 shows that under the given reaction conditions the oil yield of coprocessing determined experimentally is not only much higher than suggested by the theoretical calculation on the basis of the result obtained in separate hydrogenation of residual oils and coal; in absolute figures, it is even comparable to the oil yield in residual oil conversion.

Due to the oil yields which in practical operation are higher than expected in theory we obtain a desired reduction in the quantities of hydrogenation residue and gaseous hydrocarbons. Since these gases are unwanted products which are formed by using expensive hydrogen, it can be considered another advantage of coprocessing. The synergistic behaviour was observed over the entire temperature range and with varying reactor throughputs, and it was verified under all reaction conditions. The synergism was all the more pronounced, the smaller the reactor throughput was. This effect may be due to the heavy metal contents in the residual oil. The heavy metals can be expected to have a catalytic effect on lignite liquefaction as well. It is also conceivable that lignite or its ash will catalytically act on residual oil hydrogenation.

In the course of our work on coprocessing we determined not only the yield distribution and the quality of the products; furthermore, we critically examined the operating performance of the plant, especially in respect of coke deposits.

During coprocessing no coke deposits were observed in the reactors. Neither did we detect the formation of calcium carbonate-containing sediments known from lignite liquefaction. Obviously, the residual oil which can carry the solids particles away prevents the formation of deposits in the reaction zone which have always given rise to coking. During the above investigations of lignite liquefaction a similar effect was produced by partial recycling of the hot separator sludge.

As already mentioned, coprocessing compared with coal liquefaction alone has the considerable advantage of making slurry oil cycling superfluous. In coprocessing, the residual oil acts as slurry oil that, on its part, is converted into lower-boiling products. In the case of lignite liquefaction, the portion of cycle oil amounts to some 1.5 t per tonne of dry lignite fed. As an "inert flow" this portion takes up a major part of the reactor volume which in the case of coprocessing can be utilized for further conversion.

This permits higher specific conversion rates relative to the reaction volume. Therefore, coprocessing is expected to reach its commercial viability earlier than coal liquefaction.

Figure 9 shows in quantitative terms how the reaction volume is utilized for lignite liquefaction, hydrogenation of residual oil and coprocessing. The mass flows specified for feed and oil yield are quantities related to the same reaction volume, and thus specific quantities. Two results are given for coprocessing. On the one hand, it is the yield distribution obtained in the process development unit, and, on the other hand, the result achieved by way of theoretical calculation. The oil yield which in practical operation is higher than expected in theory can be attributed to a synergistic cooperation

of the components of lignite and residual oils. For the sake of comparison, Figure 9 shows the data of a "two-liquid-phase mode" obtained in two separate plants of the same size for coal liquefaction and residual oil hydrogenation.

The comparison of the relative specific oil yields shown in Figure 9 illustrates the considerable advantage of coprocessing over coal liquefaction alone. In coprocessing, the specific oil yield determined experimentally is 3.5 times higher than in coal liquefaction. In a theoretical calculation, a value of 3.2 is obtained.

When compared with the "two-liquid-phase mode", coprocessing has some advantages as well. For example, the relative oil yield is 3.2 (theoretical) and 3.5 (practical) as against 2.3 in the case of the "two-liquid-phase mode".

Apart from the advantages of coprocessing mentioned before account must be taken of the fact that the quality of the oils produced is slightly inferior to that from residual oil conversion alone. Depending on the boiling range and conversion rate, the oils still contain oxygen of up to about 2% wt. Due to the oxygen content of lignite and the increased formation of gaseous hydrocarbons during lignite liquefaction it is quite understandable that the chemical H_2 consumption in coprocessing is somewhat higher than for residual oil hydrogenation.

In order to corroborate the findings gained so far the coprocessing tests on a process-development scale will be continued within the scope of a follow-up project financially supported by the Federal Ministry of Research and Technology.

8 OUTLOOK

Hydrogenation of residual oil and coprocessing have the advantage of producing an oil yield in a liquid-phase plant of the same size which is about three times higher than in the case of coal hydrogenation alone. This is due to the fact that cycling of slurry oil is no longer required. Almost the entire feedstock can be processed into usable products.

If we compare plant sizes and process steps required for liquid-phase hydrogenation of residual oils from mineral oil processing and those for mixtures of dry lignite and residual oils with hydrogenation of lignite alone, the result will be as follows:

- processing of mixtures of dry lignite and residual oils calls for additional process stages, viz. slurrying and waste water treatment;
- due to a throughput which is about three times higher in coprocessing than in lignite hydrogenation alone, coprocessing permits the use of downstream conversion steps with comparable dimensions to those required for downstream conversion of residual oils;
- thus, coprocessing will call for lower specific capital expenditure than hydrogenation of lignite alone.

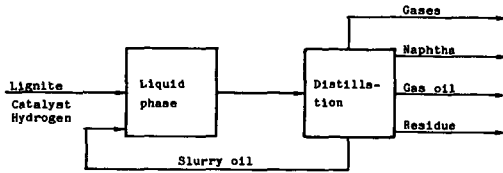
Figure 10 gives a qualitative comparison of the product costs arising in lignite hydrogenation, coprocessing and residual oil hydrogenation as a function of the costs arising for the feedstock.

Figure 10 shows that residual oil hydrogenation will reach the threshold of profitability earlier than coprocessing, while hydrogenation of lignite alone which might become a potentially important market for coal in future, will probably take much longer to reach profitability.

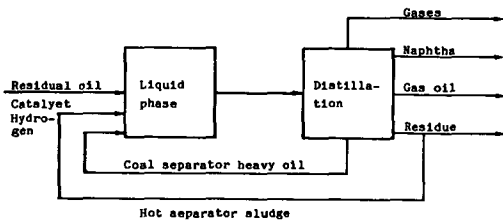
In addition, Figure 10 shows that with the relatively expensive residual oil and the relatively low-priced coal coprocessing will involve lower product costs than residual oil hydrogenation.

This expected graduation in time is reflected in the development programme on hydrogenation of fossil raw materials, which has been pursued by Rheinbraun and Union Kraftstoff. As a first step, a liquid-phase hydrogenation plant is planned for residual oil. In a second step, this plant can be extended to permit coprocessing. Coprocessing will allow important experience to be gained which is necessary to take the subsequent third step towards hydrogenation of lignite alone, without requiring great expenditure on a separate pilot or demonstration phase for lignite liquefaction.

I. FUNDAMENTAL PROCESS DIFFERENCES



II. OLD LIQUID PHASE



III. NEW LIQUID PHASE

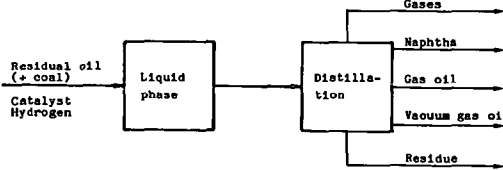


Fig. 1: FUNDAMENTAL PROCESS DIFFERENCES

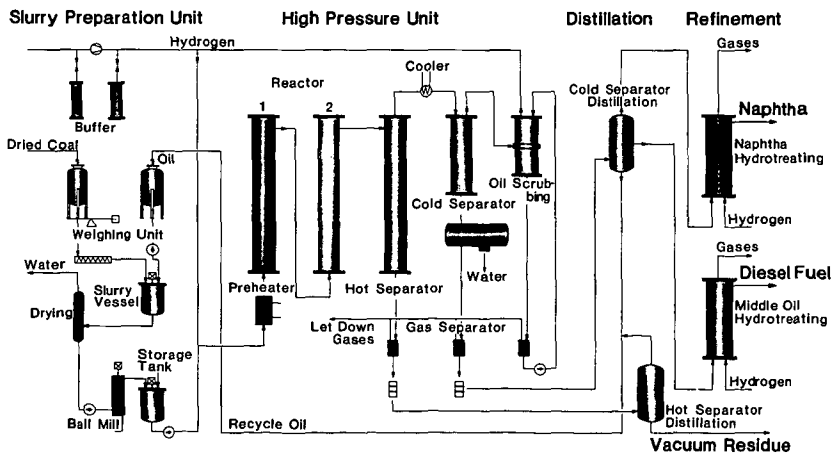


Fig. 2: FLOW SHEET OF THE HVB - TEST PLANT

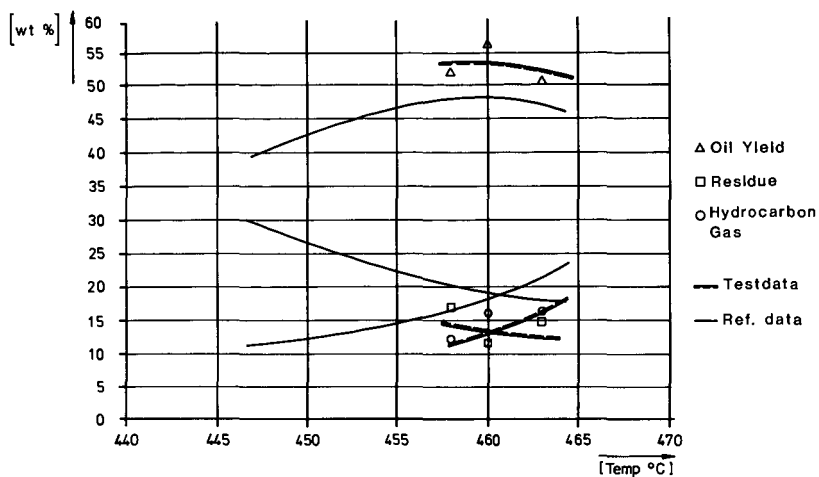


Fig. 3: YIELD AS A FUNCTION OF TEMPERATURE AND GAS INJECTION RATE

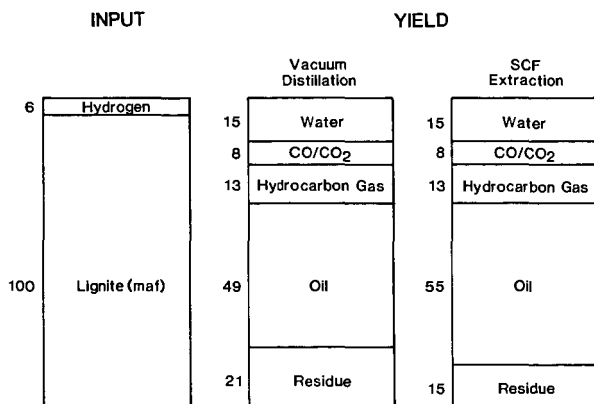


Fig. 4: COMPARISON OF PRODUCT DISTRIBUTION

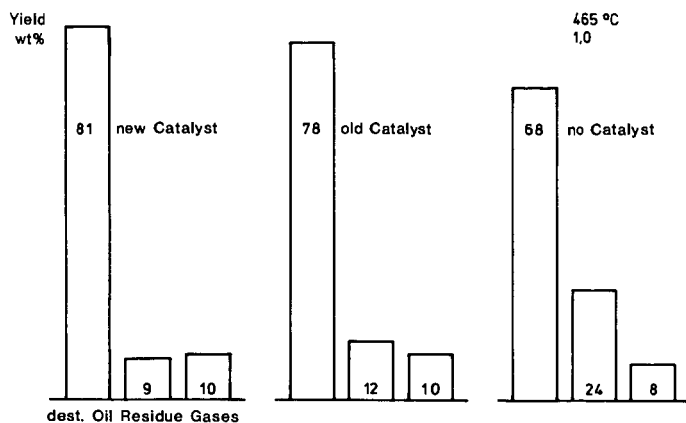


Fig.5: YIELD STRUCTURE AS A RESULT OF RESIDUAL OIL CONVERSION IN THE PRESENCE OF DIFFERENT CATALYSTS

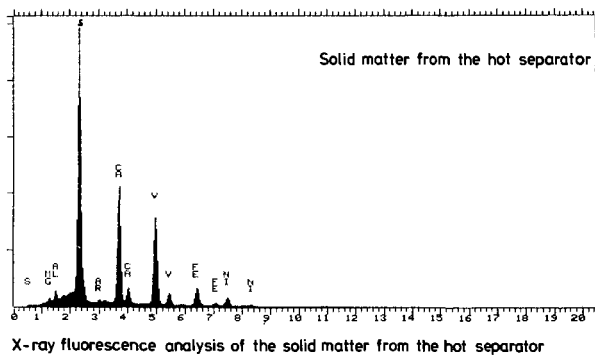
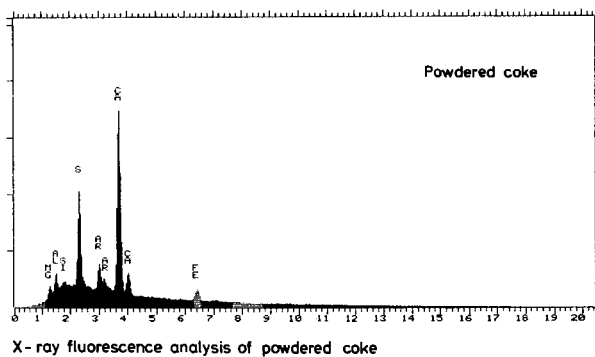


Fig.6: X- RAY FLUORESCENCE ANALYSIS

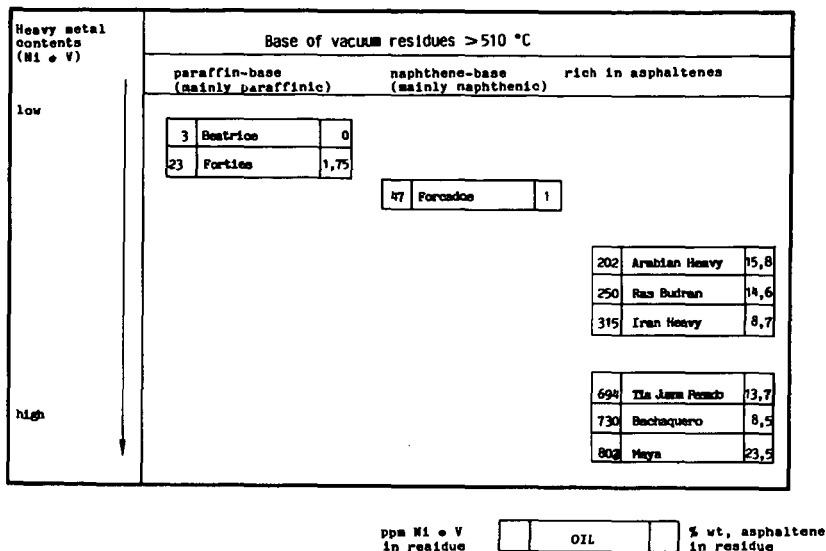


Fig.7: CHARACTERIZATION OF RESIDUAL OILS

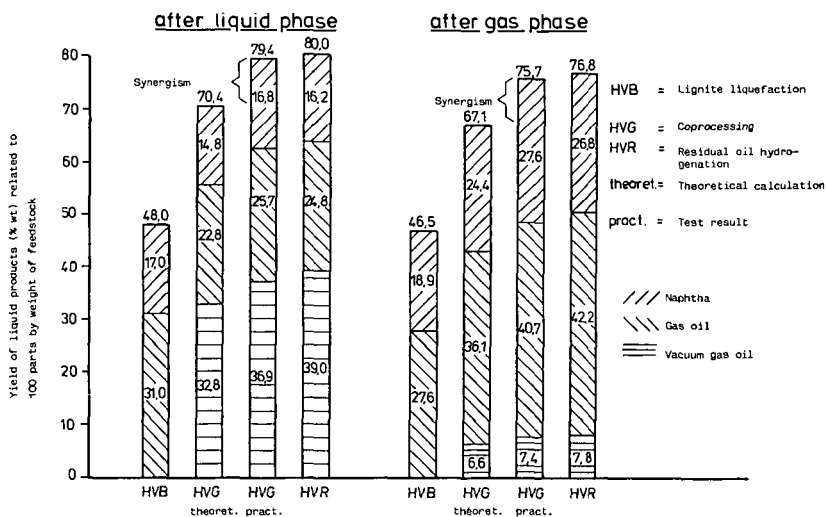


Fig. 8: OIL YIELDS IN HYDROGENATION OF RESIDUAL OILS, LIGNITE AND MIXTURES OF BOTH

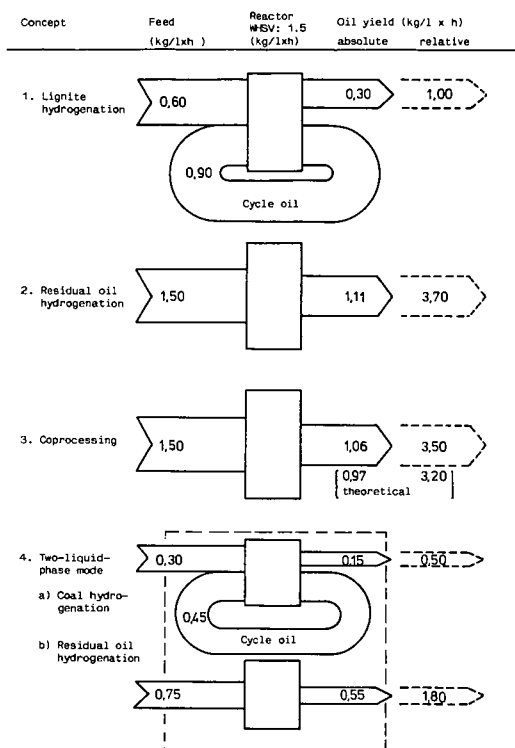


Fig.9 : PROCESS CONCEPTS

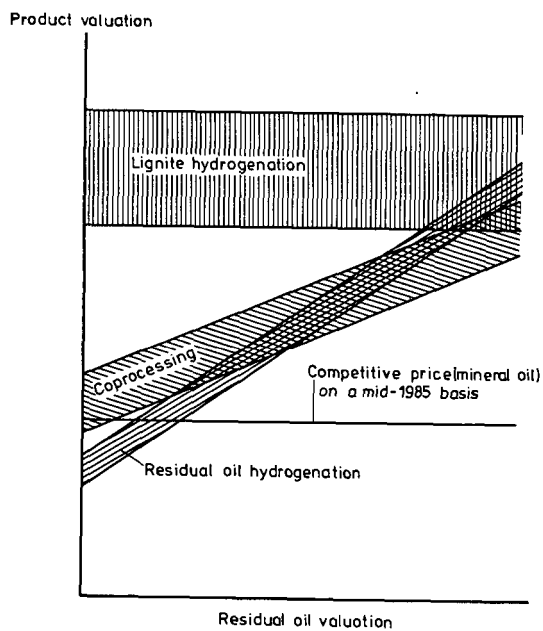


Fig.10 : PRODUCT COSTS AS A FUNKTION OF FEEDSTOCK COSTS
(QUALITATIVE)